Substitution of Mn+2 for Fe+2 in Fe-Ti Oxide Minerals: Application to Provenance Determination of Detrital Ilmenites

A Senior Honors Thesis

Presented in Partial Fulfillment of the Requirements for graduation **with distinction in Geological Sciences** in the undergraduate colleges of The Ohio State University

by

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Abstract

Ten Fe-Ti oxide grains from Wisconsinan till in Ohio, including two exhibiting exsolution lamellae, were analyzed for iron, titanium, manganese, silicon, and aluminum using an electron microprobe. The grains had a wide range of iron and titanium concentrations extending from magnetite and titanomagnetite to ilmenite and to ferrorutile. The ilmenite grains and lamellae contained $0.60 \pm 0.31\%$ MnO, which is about ten times more than the average MnO concentration of the magnetite grains ($0.06 \pm 0.04\%$).

The MnO content of ilmenites from igneous rocks in the Oslo Graben, Norway, (Neumann, 1974) increased with the silica content of the host rocks. This relationship was applied to the ilmenite grains from the Wisconsinan till in Ohio to reveal that the ilmenite from the till originated in low-silica rocks on the Precambrian shield of Canada. The result of this study was a new method of determining the possible source(s) of detrital Fe-Ti oxide grains.

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Introduction

Geologists are often confronted with the problem of determining the provenance, or place of origin, of detrital minerals in sediment such as till deposited by glaciers. Usually the method used is based on the occurrence of certain minerals having diagnostic properties, such as color. For example, if brown garnets are found in a deposit of till and in a garnet schist near the location of the till, the conclusion is made that the garnet in the till originated from that schist. In many cases, a supposition like this may be correct, but the use of diagnostic minerals such as garnet, tourmaline, and zircon can sometimes mislead a geologist because these minerals occur in many different rock types. Therefore, there is a need to develop a more reliable method of determining the source of detrital mineral grains.

Iron-titanium (Fe-Ti) oxides are attractive for this purpose because they are characteristically resistant to weathering, have high specific gravities, and are magnetic. Minerals that are resistant to weathering are likely to survive transportation from great distances and consequently will be present in amounts sufficient for analysis. In addition, Fe-Ti oxides have high specific gravities (4.18-5.18 g/cm^3), so they can be easily separated from less dense grains by immersion in a heavy liquid such as bromoform. Thirdly, the magnetism of Fe-Ti oxides allows them to be extracted using a magnetic separator.

I chose to study Fe-Ti oxide grains from Wisconsinan till in Ohio because the sources of these grains in the igneous and metamorphic rocks of the Precambrian shield of Canada are unknown. Previous work by Neumann (1974) suggested that the Mn concentration of ilmenites from the igneous rocks of the Oslo region in Norway depends on the chemical composition of the rocks from which the ilmenite originated. Therefore, I decided to investigate the distribution of manganese in Fe-Ti oxide grains of till of Ohio in order to develop a method that will help to identify the rock types from which these oxide grains originated.

Analytical Methods

The Fe-Ti oxide grains were extracted from Wisconsinan till recovered from a one-meter pit in Dover Township, Union County, Ohio (Place, 1992). Prior to removing the Fe-Ti oxide grains, the till was leached of calcite by hydrochloric acid. Then, the remaining mixture was sieved to obtain grains having diameters between 63 and 1000 micrometers. The grains were immersed in bromoform (sp. gr. 2.83 g/cm3) to separate the dense minerals such Fe-Ti oxides from grains such as quartz and feldspar. The Fe-Ti oxide grains were then extracted from the dense minerals by scanning the mixture with a hand-held magnet. The magnet was covered with a plastic sheet which allowed the Fe-Ti oxide grains to be recovered when the magnet was removed from the plastic cover. Place (1992) provided a more detailed description of this procedure.

The grains were analyzed in the Department of Geological Sciences of The Ohio State University for manganese, titanium, silicon, iron, and aluminum using an electron microprobe (Cameca Model SX-50) supplied with four wavelength-dispersive spectrometers and one energy-dispersive spectrometer. Analysis for iron and manganese required a lithium fluoride crystal (LIF), titanium required thallium hydrogen phthalate (TAP), and silicon and aluminum required the use of a penta-erythritol (PET) crystal. The analyses were conducted at 1 micron spots at 15 kv and a current of 20 na. In addition, the analyses were corrected for background, absorption and fluorescence of secondary x-rays using Cameca PAP software. The microprobe was calibrated using three standards: a magnetite standard USNM #114887 (Smithsonian Institution) was used for iron, an ilmenite standard USNM #96189 (Smithsonian Institution) was used for titanium and manganese, and a basaltic glass (Open University) was used for silicon and aluminum.

At least three different locations on each grain (except Grain 10) were analyzed by the microprobe. Grains 2, 6, 9, and 10 were homogenous magnetites, Grains 1, 3, 4, 5, and 8 were heterogeneous titanomagnetites, and Grain 7 was a homogeneous ilmenite grain. For homogenous grains the three spot analyses were averaged.

Prior to the analysis, the grains were mounted by placing them within an aluminum ring about 2 cm in diameter and pouring in epoxy to encase the grains. After the epoxy had hardened, the grains were polished to provide a flat surface for the electron beam. The grains were coated with a layer of carbon approximately 25 nm thick using a standard carbon-coating device.

Stoichiometric Composition of the Fe-Ti Oxides

Table 1 displays microprobe analyses of the chemical compositions of the Fe-Ti oxide grains extracted from Wisconsinan till in Union County, Ohio. Table 2 shows how these analyses were converted to moles of each element per 3 moles of oxygen for ilmenite and 4 moles of oxygen for magnetite. Stoichiometric formulas for the ilmenite and magnetite grains are listed in Table 3.

For the purpose of this project I consider magnetite (Fe_3O_4) to consist of at least 97% total iron expressed as FeO. The concentration of TiO_2 in ilmenite, which has the composition $FeTiO_3$, is 52.7%. Grains containing 46 to 52.7% TiO_2 are sufficiently enriched in TiO_2 to be classified as ilmenite.

Ilmenite

Table 2 column 1 lists the concentrations in weight percent of each oxide as measured by the microprobe. The sum of these concentrations do not add up to exactly 100%, so the individual percentages of the oxides must by adjusted, or normalized, so that the oxides will add up to 100%. For example, the chemical analysis of Grain (1, 1il) shows a sum of weight percents of 100.76%. To recalculate the weight percent MnO, for instance, the percent MnO is divided by the sum of the oxides and then multiplied by 100%. Column 2 displays these recalculated percentages.

We assume that the percent concentrations are equal to the number of grams of each oxide per 100 grams of sample. Thus, if the number of grams of an oxide per 100 grams is divided by the molecular weight of the oxide, the result is the number of moles of that oxide per 100 grams of sample shown in column 3.

To determine the number of moles of the individual cations per 100 grams of the sample, the number of moles of the oxide is multiplied by the number of cations in the oxide. For example, since MnO contains one manganese cation, the number in column 3 is multiplied by one, leaving the result in column 4, e.g. 0.0131 moles of MnO contain 0.0131 moles of Mn. The number of moles of oxygen is calculated similarly by

TABLE 1. Summary of chemical analyses of Fe- and Ti-oxide grains in Wisconsinan till, Union County, Ohio, in weight percent.

sample	MnO	TiO2	SiO2	FeO	Al2O3	sum
Ilmenite standard	3.317	50.996	0.043	46.56	0	100.916
Magnetite standard	1.12	2.392	0.58	95.48	0.024	99.597
Grain 1, 1tm	0.104	9.516	0.016	90.17	0.077	99.882
Grain 1, 2tm	0.309	16.778	0.027	82.402	0.027	99.543
Grain 1, 3tm	0.766	30.421	0	69.097	0	100.283
Grain 1, 4tm	4.676	42.172	0.063	54.562	0	101.473
Grain 1, 1fr	0.313	61.147	0.048	36.933	0	98.442
Grain 1, 1il	0.936	48.203	0.06	51.561	0	100.76
Grain 2, 1m	0.001	0.062	0.054	99.431	0.291	99.84
Grain 2, 2m	0	0.006	0.271	99.836	0.385	100.498
Grain 2, 3m	0	0.05	0.687	98.616	0.706	100.061
average	0	0.039	0.337	99.294	0.461	100.133
std. dev.	0.0006	0.029	0.322	0.203	0.218	0.335
error %	173	75	95.4	0.204	47.2	0.334
Grain 3, 1tm	0.741	19.657	0.02	72.628	1.814	94.86
Grain 3, 2tm	0.748	19.718	0.046	74.973	1.996	97.481
Grain 3, 3tm	0.692	19.702	0.088	72.458	1.87	94.81
average	0.727	19.692	0.051	73.353	1.893	95.717
std. dev.	0.031	0.032	0.034	1.406	0.093	1.528
error %	4.2	0.161	66.8	1.92	4.92	1.6
Grain 4, 1tm	0.204	39.324	0.037	59.862	0	99.428
Grain 4, 2tm	1.147	12.964	0.23	79.154	0.019	93.513
Grain 4, 1il	0.328	43.974	0.105	49.657	0	94.064
Grain 4, 1fr	0.086	79.964	0.051	11.501	0	91.598

sample	MnO	TiO2	SiO2	FeO	Al2O3	sum
Grain 5, 1tm	0.504	21.152	0.103	76.789	1.69	100.238
Grain 5, 2tm	0.917	22.438	1.02	74.612	1.33	100.317
Grain 5, 3tm	0.803	26.078	0.197	73.898	1.127	102.103
average	0.741	23.223	0.44	75.1	1.382	100.886
std. dev.	0.213	2.555	0.504	1.506	0.285	1.055
error %	28.8	11	115	2	20.6	1.05
Grain 6, 1m	0.048	0.06	1.54	87.848	1.146	90.641
Grain 6, 2m	0.043	0.012	1.764	90.182	0.775	92.777
Grain 6, 3m	0.048	0.057	1.749	89.902	0.758	92.514
average	0.046	0.043	1.684	89.311	0.893	91.977
std. dev.	0.003	0.027	0.125	1.274	0.219	1.165
error %	6.23	62.5	7.43	1.43	24.6	1.27
Grain 7, 1il	0.51	48.208	0.014	55.795	0	104.528
Grain 7, 2il	0.573	47.662	0.027	54.025	0	102.287
Grain 7, 3il	0.567	47.591	0.013	55.939	0	104.11
average	0.55	47.82	0.018	55.253	0	103.642
std. dev.	0.035	0.338	0.008	1.066	0	1.192
error %	6.32	0.706	43	2	0	1.15
Grain 8, 1tm	0.331	16.625	1.968	71.594	1.162	91.68
Grain 8, 2tm	1.913	25.73	1.003	67.413	0.42	96.479
Grain 8, 3tm	0.328	13.056	1.576	74.996	1.104	91.06
Grain 9, 1m	0.111	0.03	0.036	100.549	0.113	100.839
Grain 9, 2m	0.048	0.013	0.069	101.554	0.1	101.783
Grain 9, 3m	0.104	0.058	0	100.508	0.128	100.799
average	0.088	0.034	0.035	100.87	0.114	101.14
std. dev.	0.035	0.023	0.035	0.592	0.014	0.557
error %	39	68	99	0.587	0.11	0.551
Grain 10, 1m	0.085	0.035	0.154	99.397	0.154	99.825

TABLE 2. Conversion of analyzed weight percents to number of moles of each element per 3 oxygens (ilmenite) or per 4 oxygens (magnetite).

GRAIN 1, 1il

	1	2	3		4	5
MnO	0.936	0.92894	0.0131	Mn	0.0131	0.02041
TiO2	48.203	47.83942	0.5987	Ti	0.5987	0.932797
SiO2	0.06	0.059547	0.0014	Si	0.0014	0.002181
FeO	51.561	51.17209	0.7122	Fe	0.7122	1.109634
Al2O3	0	0	0	Al	0	0
				O	1.9255	
sum	100.76	100				2.06

GRAIN 10, 1m

	1	2	3		4	5
MnO	0.085	0.085149	0.0012	Mn	0.0012	0.002579
TiO2	0.035	0.035061	0.0004	Ti	0.0004	0.00086
SiO2	0.154	0.15427	0.0035	Si	0.0035	0.007522
FeO	99.397	99.57125	0.4619	Fe+2	0.4619	0.992746
Fe2O3	n.d.	n.d.	0.4619	Fe+3	0.9238	1.985492
Al2O3	0.154	0.15427	0.0015	Al	0.003	0.006448
				O	1.8611	
sum	99.825	100				3.00

Column 1:	Weight percent as measured in oxide form
Column 2:	Weight percent recalculated to 100%
Column 3:	Moles per 100 g of mineral
Column 4:	Moles of cation per 100 g of mineral
Column 5:	Number of cations per 3 Oxygens (ilmenite) or 4 Oxygens (magnetite)

adding the number of moles of oxygen in each oxide.

Column 5 displays the number of moles of each cation per three moles of oxygen. To obtain the numbers in this column, the molar amounts of each cation in column 4 is divided by the number of moles of oxygen per 100 grams of sample (1.9255 in this example) and then multiplied by three. For example, if Mn = 0.0131 moles, then the number of moles of Mn per 3 moles of oxygen is 0.0131 / 1.9255 x 3 = 0.0204.

The results of this series of calculations are exhibited in the appendix in tables such as the one shown in Table 2.

The stoichiometric formulas can be determined from the results in column 5. Table 3A displays the stoichiometric formulas of the ilmenite grains. The concentrations of manganese and silicon are so low that the molar amounts per three moles of oxygen are both less than 0.03, and therefore these elements can be omitted from the stoichiometric formula for these ilmenites:

$$Fe_{1.1}Ti_{0.9}O_3$$

This result demonstrates that the ilmenite grains are depleted in titanium and are correspondingly enriched in iron relative to a pure ilmenite. The titanium deficiency is expected because the ilmenite grains contain less than 52.7% TiO_2. Nevertheless, these grains are classified as ilmenite.

Magnetite

Magnetite contains three cations for every four oxygens as shown in the formula Fe_3O_4. Magnetite can also be represented as $FeOFe_2O_3$, demonstrating that one of the iron cations is Fe^{+2} and two are Fe^{+3} cations. However, since the microprobe does not distinguish between different oxidation states of the same element, it is programmed to express the total iron of the magnetite grains as FeO. Consequently, before the number of moles of FeO and Fe_2O_3 per 100 g sample (column 3) can be determined, the iron must be reapportioned to include Fe^{+3} in addition to the Fe^{+2}. Because the ratio of

TABLE 3 A, B, and C. Calculation of cation to oxygen ratio for ilmenite (A) and magnetite (B). A calculation of the cation to oxygen ratio for one of the titanomagnetite grains is shown in (C) to demonstrate the lack of stoichiometry.

sample	Fe+3	Fe+2	Ti	Mn	Al	Si	sum
ILMENITE							
Gr 1, 1il	0	1.11	0.933	0.02	0	0.002	2.065
Gr 4, 1il	0	1.15	0.917	0.008	0	0.004	2.079
Gr 7, 1,2,3	0	1.17	0.909	0.012	0	0.001	2.092
average	0	1.14	0.92	0.013	0	0.002	2.075
rounded	0	1.1	0.9	0	0	0	2.0

(A)

MAGNETITE							
Gr 2, 1,2,3	1.97	0.984	0.001	0	0.019	0.016	2.99
Gr 6 1,2,3	1.88	0.941	0.001	0.002	0	0.087	2.991
Gr 9, 1,2,3	1.99	0.996	0.001	0.003	0.005	0.002	2.997
Gr 10, 1m	1.99	0.993	0.001	0.003	0.006	0.008	3.001
average	1.96	0.979	0.001	0.002	0.008	0.028	2.978
rounded	2.01	1.01	0	0	0	0	3.0

(B)

TITANOMAGNETITE							
Gr 4, 1tm	1.06	0.529	0.938	0.005	0	0.002	2.534
rounded	1.1	0.5	0.9	0	0	0	2.5

(C)

Fe^{+2} to Fe^{+3} is 1:2=, I assigned one-third of the total iron to FeO and the rest to Fe_2O_3. However, Fe_2O_3 contains two atoms of iron, so the molar amount of Fe_2O_3 is divided by two because it takes two moles of Fe^{+3} to make one mole of Fe_2O_3. A sample calculation is shown below for Grain (10, 1m).

Total iron = FeO (after recalculating the analysis to 100%)
= 99.571g (from Table 2 column 2) / (71.85g/mole) = 1.386 moles FeO
= 1.386 moles Fe

Fe2O3 = 2/3 (1.386 moles) /2 = 0.462 moles

Table 3B shows how the chemical composition of the magnetite grains is used to calculate its stoichiometric formula. According to the analysis, the magnetite contains titanium, manganese, aluminum and silicon in addition to iron. As in the ilmenite, the molar amounts of these elements relative to 4 moles of oxygen are low (less than 0.1), and were therefore omitted from the stoichiometric formula for magnetite:

$$(Fe^{+2}{}_{1.0}O)(Fe^{+3}{}_{2.0}O_3)$$

Titanomagnetite

Table 3C demonstrates what happens when the method for reapportioning the iron is applied to magnetites containing significant concentrations of titanium. The addition of varying molar amounts of TiO_2 to magnetite alters the structure of magnetites so much that it cannot be assumed to have the same chemical formula as magnetite. Consequently, when the titanomagnetites are normalized to four oxygens as in magnetite, a nonstoichiometric number of cations results. The amount of cations in the titanomagnetites per four oxygens ranged from 2.15 in Grain (1, 4tm) to 2.88 in Grain (1, 1tm). These results show that titanomagnetite does not have a stoichiometric composition because the ratio of Fe to Ti varies widely.

In order to illustrate the range of compositions of titanomagnetite, the samples are plotted in Figure 1 in coordinates of total iron expressed as FeO vs. TiO_2. The locations of magnetite, ulvospinel (Fe_2TiO_4), ilmenite, and rutile (TiO_2) are also

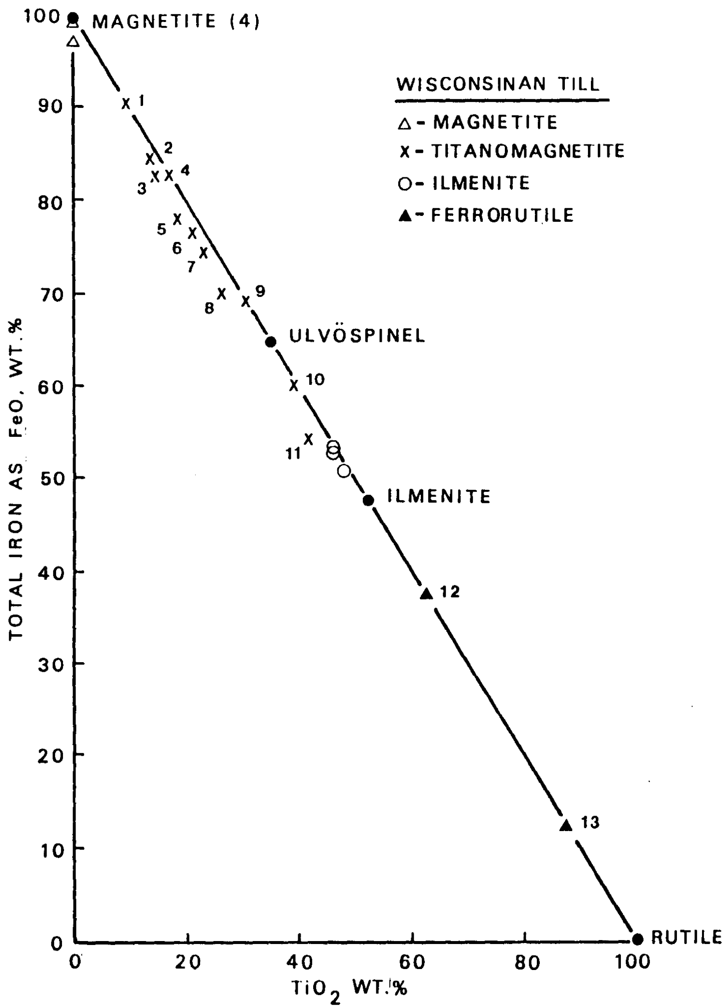

Figure 1. Distribution of Fe-Ti oxides from Wisconsinan till, Union County, Ohio, according to their iron and titanium content. A solubility gap appears at ulvospinel. Total iron is expressed as FeO.

shown for comparison. The four magnetite samples are located in the upper left at FeO=97% and TiO_2=0%. The titanomagnetites, labeled 1 thru 11, are distributed along a line drawn from magnetite, through ulvospinel and ilmenite, to rutile. The distribution of the titanomagnetites along this line demonstrates a limited solid solution between magnetite and ilmenite. Lindsley (1991) stated that a miscibility gap lies between magnetite and ulvospinel. The graph does show a gap near ulvospinel consistent with the fact that ulvospinel has not been found in nature except as exsolution lamellae in magnetite (Deer et al., 1992).

Points 12 and 13 in Figure 1, located between ilmenite and rutile, represent iron-bearing titanium oxides (ferrorutile) whose existence suggests a possible solid solution between ilmenite and rutile.

Distribution of Mn in Fe-Ti Oxides

One of the objectives of this study is to describe the distribution of manganese in the Fe-Ti oxides based on the assumption that Mn^{+2} can substitute for Fe^{+2}. Therefore, I postulate that the concentration of Mn^{+2} in Fe-Ti oxides should increase with the concentration of Fe^{+2}.

First we compare the ionic radius of manganese with those of the three cations it might replace in Fe-Ti oxides.

	Ionic Radius(A = 10^{-8}cm)	Electronegativity
Mn^{+2}	0.80 A	1.5
Fe^{+2}	0.76 A	1.8
Ti^{+4}	0.68 A	1.5
Fe^{+3}	0.64 A	1.8

According to Goldschmidt's rules, two cations can substitute for each other extensively if their radii differ by less than 15%. The radius of Mn^{+2} differs from the radius of

Fe^{+2} by only 5%, whereas it differs from Ti^{+4} by 18% and Fe^{+3} by 25%. Therefore, Mn^{+2} should only substitute extensively for Fe^{+2}.

Next we compare the charges of the cations. Cations will only substitute extensively for one another if their charges are identical. Mn^{+2} has a different charge than Fe^{+3}, and there is an even greater charge difference between Mn^{+2} and Ti^{+4}; thus, Mn^{+2} should not substitute for these cations. However, Mn^{+2} and Fe^{+2} are both divalent cations, so the Mn^{+2} can substitute for the Fe^{+2}.

Additionally, in order for one cation to substitute for another, the cations must have similar electronegativities so that they form similar bonds. In oxides, the cations form bonds with oxygen, which has an electronegativity of 3.5. Calculating the electronegativity difference between oxygen and iron yields 1.7, which in turn yields a percent ionic character of 51% for the Fe-O bond (Sargent-Welch, 1980). Therefore, a cation needs to have a percent ionic character similar to 51% in order to substitute for iron. The electronegativity difference between manganese and oxygen is 2.0, resulting in 63% ionic character for the Mn-O bond, which is a discrepancy low enough to permit manganese to replace iron.

This review of the relevant principles of crystal chemistry leads to the expectation that ilmenite should have a higher manganese content than magnetite because all iron in ilmenite is Fe^{+2} and only one-third of the iron in magnetite is Fe^{+2}. This point is illustrated by the fact that the mineral pyrophanite ($MnTiO_3$), which forms when all the Fe^{+2} in ilmenite is replaced by manganese, contains 47% MnO, whereas in the mineral jacobsite ($MnFe_2O_4$), magnetite in which all Fe^{+2} is replaced by manganese, the MnO concentration is only 31%.

In addition, the average MnO concentration of the magnetites analyzed in this study (Table 4) is 0.06 ± 0.04%, whereas the MnO content of the ilmenites is 0.60 ± 0.31%. Evidently, the ilmenite grains contain about 10 times more MnO than the magnetite grains. This evidence supports the conclusion that manganese substitutes preferentially for Fe^{+2}.

To further illustrate that Mn^{+2} substitutes for Fe^{+2}, I plotted in Figure 2 the analyses of magnetite and ilmenite grains from igneous rocks in the Oslo Graben of Norway (Neumann, 1974). These minerals show a range of compositions from magnetite to near ulvospinel, indicating that many of these grains are actually titanomagnetites. The solubility gap discussed earlier appears near ulvospinel in the same location as in Figure 1, which is based on my data from Wisconsinan till in Ohio. Most importantly, however, Figure 2 shows that the ilmenites from the Oslo Graben are depleted in FeO but maintain an essentially constant TiO_2 content. Therefore, another cation must be substituting for the iron in the ilmenites.

The substituting cation is likely to be manganese as previously discussed. Therefore, in Figure 3 the MnO content of the Norwegian ilmenites and magnetites is plotted versus total iron as FeO. The resulting diagram demonstrates that the MnO concentration of the magnetites (total iron as FeO greater than 97%) is less than 1% whereas that of the ilmenites ranges up to nearly 31%. Titanomagnetites have intermediate concentrations of MnO, and ulvospinel marks the solubility gap. Figures 2 and 3 demonstrate an inverse correlation between the total iron as FeO and the MnO content. For example, ilmenite #1 contains the lowest concentration of total iron and the highest concentration of MnO, whereas ilmenite #6 contains the highest concentration of iron and the lowest concentration of MnO. Therefore, this comparison confirms that manganese substitutes extensively for Fe^{+2} in ilmenite but only to a limited extent in magnetite, which contains twice as much Fe^{+3} as Fe^{+2}.

A plot of MnO concentration versus total iron as FeO for the grains from the

TABLE 4. Average MnO concentrations in ilmenite and magnetite in Wisconsinan till of Ohio.

	sample	MnO wt.%
ILMENITE		
	Gr 1, 1il	0.936
	Gr 4, 1il	0.328
	Gr 7, 1,2,3	0.55
	average	0.60 + 0.31
MAGNETITE		
	Gr 2, 1,2,3	0
	Gr 5, 1,2,3	0.046
	Gr 9, 1,2,3	0.088
	Gr 10, 1m	0.085
	average	0.06 + 0.04

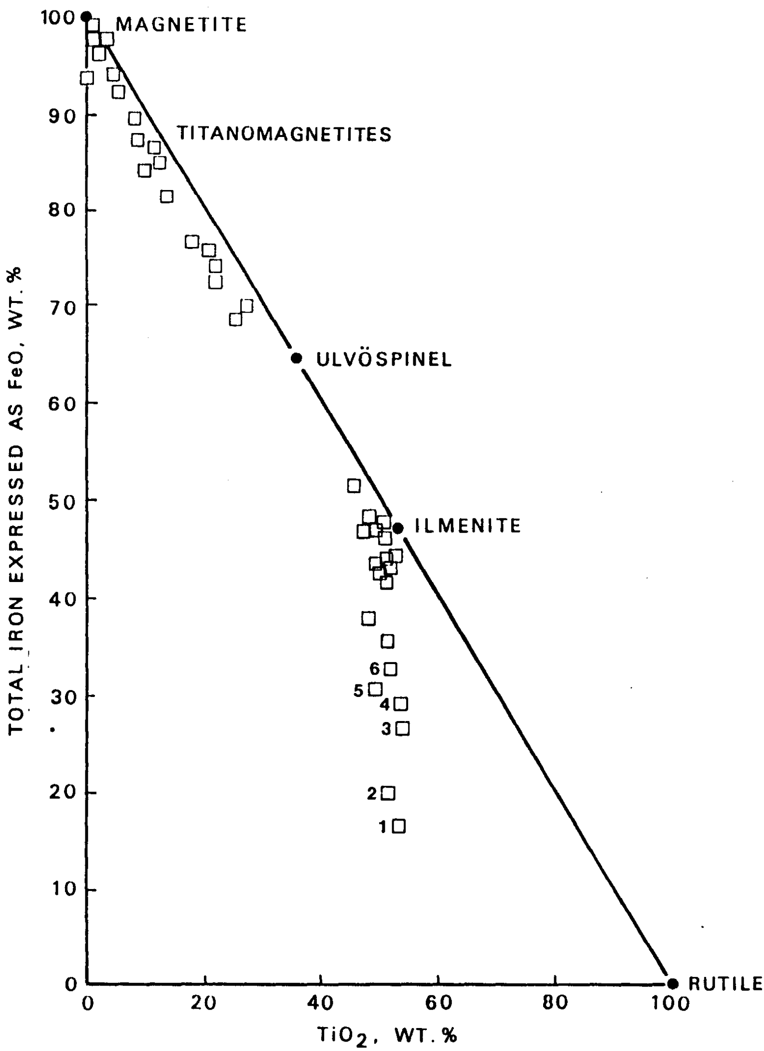

Figure 2. Distribution of Fe-Ti oxides from igneous rocks in the Oslo Graben of Norway (Neumann, 1974) according to their iron and titanium content. Total iron is expressed as FeO.

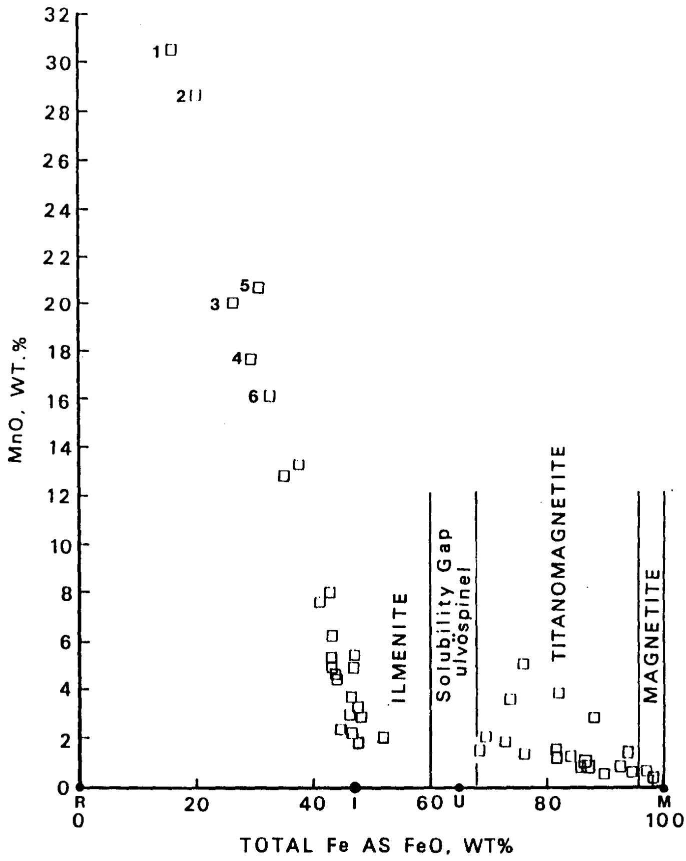

Figure 3. Concentration of manganese in Fe-Ti oxides from igneous rocks in the Oslo Graben of Norway (Neumann, 1974). Total iron is expressed as FeO.

Wisconsinan till in Figure 4 shows the same tendency. The manganese content of rutile is very low, which is expected because rutile contains no iron. The MnO content increases from rutile through ferrorutile and ilmenite to ferroan ilmenite, where it reaches 4.6%. On the other side of the ulvospinel solubility gap, the MnO content decreases from titanomagnetite to magnetite as the proportion of Fe^{+3} to Fe^{+2} increases. A curve representing the apparent saturation limit for manganese in Fe-Ti oxides is drawn through the points which show the highest concentrations of manganese for their iron content. Any points that fall below this curve presumably represent Fe-Ti oxides that formed in rocks that did not contain enough manganese to allow substitution to occur to its maximum extent.

Accordingly, we expect the MnO concentration of Fe-Ti oxide minerals to be linked to the type of rock from which they came. Therefore, in Figure 5, the MnO concentration of ilmenite grains from the Oslo Graben is plotted versus the SiO_2 content of their corresponding host rocks. The data points define a curve showing that the MnO content of the ilmenite increases with increasing silica content in the host rock. Granites, which contain 70% or more silica, contain more manganese in their ilmenite grains than rocks such as gabbros, peridotites, or komatiites, which consist of about 50% silica. Thus, given any ilmenite grain, it is possible to determine its provenance simply by analyzing the ilmenite for its MnO concentration. The ilmenite from the Ohio till contains $0.60 \pm 0.31\%$ MnO, which indicates that the SiO_2 content of its host rock was very low; therefore, the source was rock such as gabbro, peridotite, and komatiite.

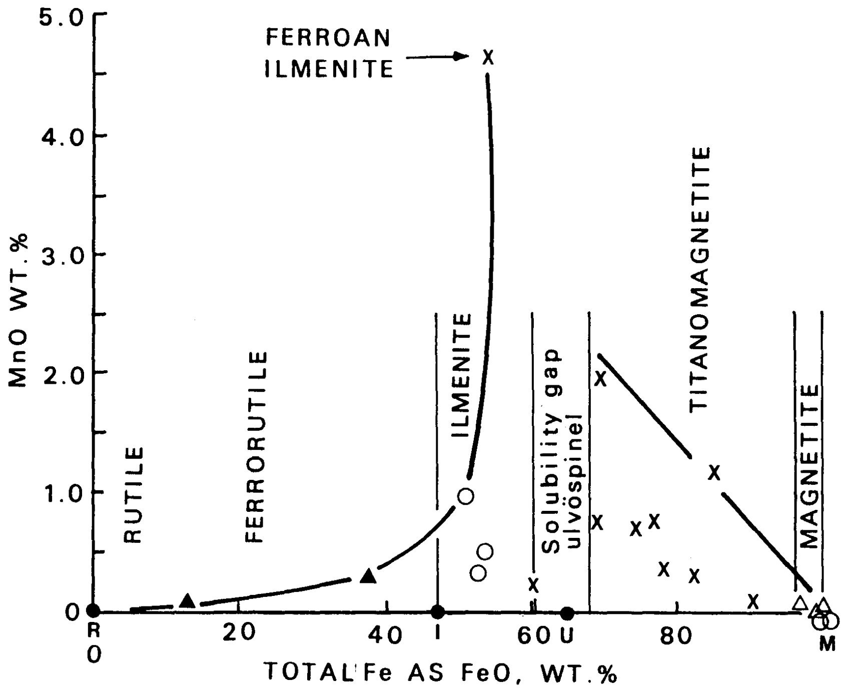

Figure 4. Concentration of manganese in Fe-Ti oxides in Wisconsinan till, Union County, Ohio. Total iron is expressed as FeO.

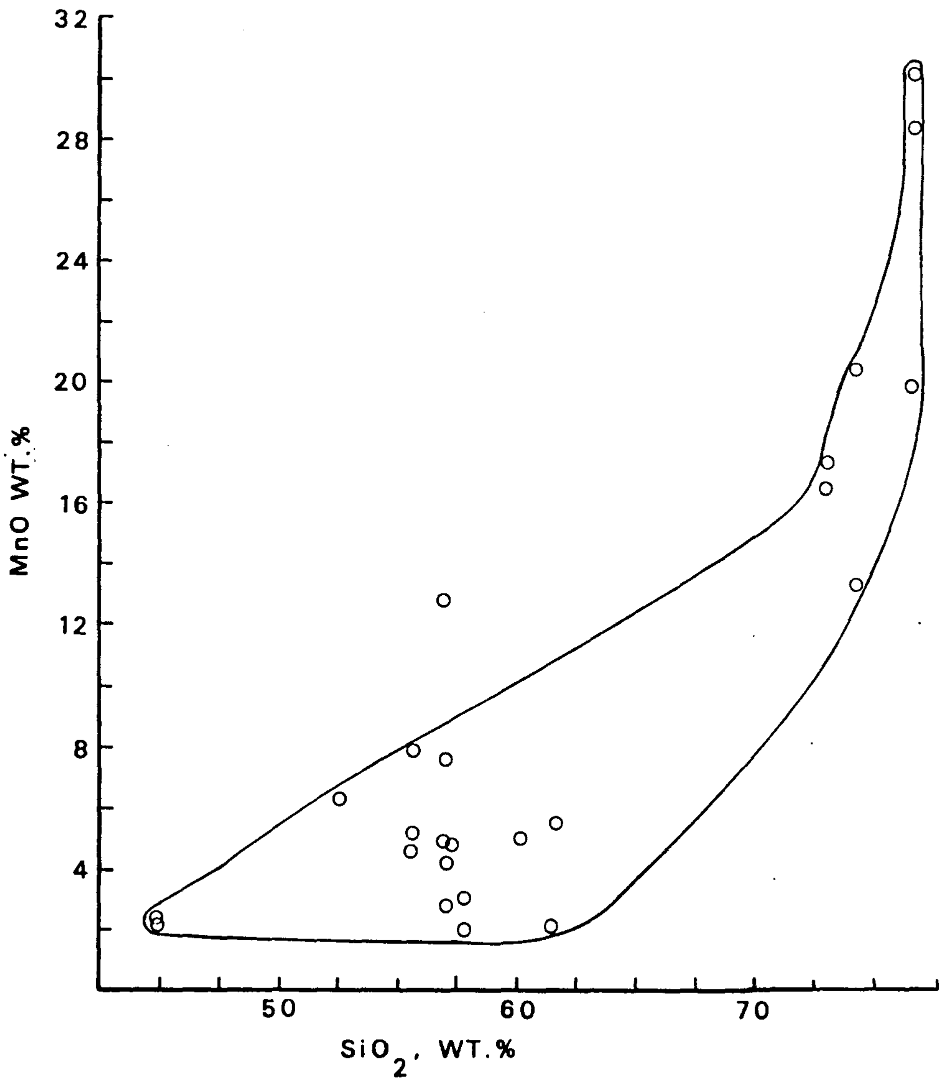

Figure 5. Concentration of manganese in ilmenites from igneous rocks in the Oslo Graben, Norway, in relation to the silica content of the host rocks (Neumann, 1974).

Summary of Conclusions

The prime objective of this study was to develop a reliable method of determining the possible source(s) of detrital mineral grains. The Fe-Ti oxides were chosen for study because their manganese content was expected to result by replacement of Fe^{+2} and because the manganese concentrations of ilmenite grains are related to the SiO_2 content of the igneous rocks from which the grains originated.

I have shown that grains of Fe-Ti oxides from Wisconsinan till of Ohio have a range of iron and titanium concentrations extending from magnetite and titanomagnetite to ilmenite and from ilmenite to ferrorutile. In addition, the ilmenite grains contained 0.60±0.31% MnO, which is about ten times as much MnO as the magnetite grains (0.06±0.04%).

Previous work by Neumann (1974) suggested that the MnO content of ilmenites from igneous rocks in the Oslo Graben of Norway increases with the silica content of the host rocks. This relationship suggests that if the ilmenite has a low MnO content, the host rock of the ilmenite grain has a low silica content. The ilmenite grains from Wisconsinan till have a low MnO content, thus indicating that the host rocks of these grains were gabbro or some such low-silica igneous rocks. Therefore, this study has successfully demonstrated a new method of determining the provenance of detrital ilmenite grains.

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ILMENITE

GRAIN 1, 1il

	1	2	3		4	5
MnO	0.936	0.9289	0.0131	Mn	0.0131	0.0204
TiO2	48.203	47.839	0.5987	Ti	0.5987	0.9328
SiO2	0.06	0.0595	0.0014	Si	0.0014	0.0022
FeO	51.561	51.172	0.7122	Fe	0.7122	1.1096
Al2O3	0	0	0	Al	0	0
				O	1.9255	
sum	100.76	100				2.06

GRAIN 4, 1il

	1	2	3		4	5
MnO	0.328	0.3487	0.005	Mn	0.005	0.0078
TiO2	43.974	46.749	0.585	Ti	0.585	0.9166
SiO2	0.105	0.1116	0.0025	Si	0.0025	0.0039
FeO	49.657	52.791	0.7347	Fe	0.7347	1.1511
Al2O3	0	0	0	Al	0	0
				O	1.9147	
sum	94.064	100				2.08

GRAIN 7, 1,2,3

	1	2	3		4	5
MnO	0.55	0.5307	0.0075	Mn	0.0075	0.0118
TiO2	47.82	46.14	0.5775	Ti	0.5775	0.9093
SiO2	0.018	0.0174	0.0004	Si	0.0004	0.0006
FeO	55.253	53.311	0.742	Fe	0.742	1.1683
Al2O3	0	0	0	Al	0	0
				O	1.9053	
sum	103.64	100				2.09

MAGNETITE

GRAIN 2, 1,2,3

	1	2	3		4	5
MnO	0	0	0	Mn	0	0
TiO2	0.039	0.0389	0.0005	Ti	0.0005	0.0011
SiO2	0.337	0.3366	0.0076	Si	0.0076	0.0163
FeO	99.294	99.162	0.46	Fe+2	0.46	0.9841
Fe2O3	n.d.	n.d.	0.46	Fe+3	0.92	1.9682
Al2O3	0.461	0.4604	0.0045	Al	0.009	0.0193
				O	1.8697	
sum	100.13	100				2.99

GRAIN 6, 1,2,3

	1	2	3		4	5
MnO	0.046	0.05	0.0007	Mn	0.0007	0.0015
TiO2	0.043	0.0468	0.0006	Ti	0.0006	0.0013
SiO2	1.684	1.8309	0.0415	Si	0.0415	0.0867
FeO	89.311	97.101	0.4505	Fe+2	0.4505	0.9408
Fe2O3	n.d.	n.d.	0.4505	Fe+3	0.901	1.8816
Al2O3	0.893	0.9709	0.0095	Al	0.019	0.0397
				O	1.9154	
sum	91.977	100				2.95

GRAIN 9, 1,2,3

	1	2	3		4	5
MnO	0.088	0.087	0.0012	Mn	0.0012	0.0026
TiO2	0.034	0.0336	0.0004	Ti	0.0004	0.0009
SiO2	0.035	0.0346	0.0008	Si	0.0008	0.0017
FeO	100.87	99.733	0.4627	Fe+2	0.4627	0.9963
Fe2O3	n.d.	n.d.	0.4627	Fe+3	0.9254	1.9926
Al2O3	0.114	0.1127	0.0011	Al	0.0022	0.0047
				O	1.8577	
sum	101.14	100				3.00

GRAIN 10, 1m

	1	2	3		4	5
MnO	0.085	0.0851	0.0012	Mn	0.0012	0.0026
TiO2	0.035	0.0351	0.0004	Ti	0.0004	0.0009
SiO2	0.154	0.1543	0.0035	Si	0.0035	0.0075
FeO	99.397	99.571	0.4619	Fe+2	0.4619	0.9927
Fe2O3	n.d.	n.d.	0.4619	Fe+3	0.9238	1.9855
Al2O3	0.154	0.1543	0.0015	Al	0.003	0.0064
				O	1.8611	
sum	99.825	100				3.00

TITANOMAGNETITE AND FERRORUTILE

GRAIN 1, 1tm

	1	2	3		4	5
MnO	0.104	0.1041	0.0015	Mn	0.0015	0.0031
TiO2	9.516	9.5272	0.119	Ti	0.119	0.2481
SiO2	0.016	0.016	0.0004	Si	0.0004	0.0008
FeO	90.17	90.277	0.419	Fe+2	0.419	0.8736
Fe2O3	n.d.	n.d.	0.419	Fe+3	0.838	1.7472
Al2O3	0.077	0.0771	0.0008	Al	0.0015	0.0031
				O	1.9185	
sum	99.882	100				2.88

GRAIN 1, 2tm

	1	2	3		4	5
MnO	0.309	0.3104	0.0044	Mn	0.0044	0.0089
TiO2	16.778	16.855	0.211	Ti	0.211	0.4296
SiO2	0.027	0.0271	0.0006	Si	5	0.0013
FeO	82.402	82.78	0.384	Fe+2	0.384	0.7819
Fe2O3	n.d.	n.d.	0.384	Fe+3	0.768	1.564
Al2O3	0.027	0.0271	0.0003	Al	0.0005	0.0011
				O	1.9644	
sum	99.543	100				2.79

GRAIN 1, 3tm

	1	2	3		4	5
MnO	0.766	0.764	0.0108	Mn	0.0108	0.0211
TiO2	30.421	30.335	0.38	Ti	0.38	0.7417
SiO2	0	0	0	Si	0	0
FeO	69.097	68.902	0.32	Fe+2	0.32	0.6246
Fe2O3	n.d.	n.d.	0.32	Fe+3	0.639	1.2472
Al2O3	0	0	0	Al	0	0
				O	2.0494	
sum	100.28	100				2.63

GRAIN 1, 1tml

	1	2	3		4	5
MnO	4.676	4.6081	0.065	Mn	0.065	0.1051
TiO2	42.172	41.56	0.52	Ti	0.52	0.8404
SiO2	0.063	0.0621	0.0014	Si	0.0014	0.0023
FeO	54.562	53.77	0.7484	Fe+2	0.7484	1.2096
Fe2O3	n.d.	n.d.	n.d.	Fe+3	n.d.	n.d.
Al2O3	0	0	0	Al	0	0
				O	1.8562	
sum	101.47	100				2.16

GRAIN 1, 1frl

	1	2	3		4	5
MnO	0.313	0.318	0.0045	Mn	0.0045	0.0065
TiO2	61.147	62.113	0.7774	Ti	0.7774	1.1193
SiO2	0.048	0.049	0.0011	Si	0.0011	0.0016
FeO	36.933	37.517	0.5222	Fe+2	0.5222	0.7518
Fe2O3	n.d.	n.d.	n.d.	Fe+3	n.d.	n.d.
Al2O3	0	0	0	Al	0	0
				O	2.0837	
sum	98.442	100				1.88

GRAIN 3, 1,2,3

	1	2	3		4	5
MnO	0.727	0.7595	0.0107	Mn	0.0107	0.0213
TiO2	19.692	20.573	0.2575	Ti	0.2575	0.5128
SiO2	0.051	0.0533	0.0012	Si	0.0012	0.0024
FeO	73.353	76.635	0.3556	Fe+2	0.3556	0.7081
Fe2O3	n.d.	n.d.	0.3556	Fe+3	0.7112	1.4162
Al2O3	1.893	1.9777	0.0194	Al	0.0388	0.0773
				O	2.0087	
sum	95.717	100				2.74

GRAIN 4, 1tm

	1	2	3		4	5
MnO	0.204	0.205	0.0029	Mn	0.0029	0.0055
TiO2	39.324	39.55	0.495	Ti	0.495	0.9376
SiO2	0.037	0.037	0.0008	Si	0.0008	0.0015
FeO	59.862	60.206	0.2793	Fe+2	0.2793	0.5291
Fe2O3	n.d.	n.d.	0.2793	Fe+3	0.5586	1.0581
Al2O3	0	0	0	Al	0	0
				O	2.1117	
sum	99.428	100				2.53

GRAIN 4, 2tm

	1	2	3		4	5
MnO	1.147	1.227	0.0173	Mn	0.0173	0.0367
TiO2	12.964	13.863	0.1735	Ti	0.1735	0.3684
SiO2	0.23	0.246	0.0056	Si	0.0056	0.0118
FeO	79.154	84.645	0.377	Fe+2	0.377	0.8004
Fe2O3	n.d.	n.d.	0.377	Fe+3	0.7539	1.6008
Al2O3	0.019	0.02	0.0002	Al	0.0004	0.0008
				O	1.8838	
sum	93.513	100				2.82

GRAIN 4, 1frl

	1	2	3		4	5
MnO	0.086	0.0939	0.0013	Mn	0.0013	0.0017
TiO2	79.964	87.299	1.0926	Ti	1.0926	1.3908
SiO2	0.051	0.0557	0.0013	Si	0.0013	0.0016
FeO	11.501	12.556	0.1677	Fe+2	0.1677	0.2135
Fe2O3	n.d.	n.d.	n.d.	Fe+3	n.d.	n.d.
Al2O3	0	0	0	Al	0	0
				O	2.3568	
sum	91.598	100				1.61

GRAIN 5, 1,2,3

	1	2	3		4	5
MnO	0.741	0.7345	0.0103	Mn	0.0103	0.0178
TiO2	23.223	23.019	0.2881	Ti	0.2881	0.499
SiO2	0.44	0.4361	0.0099	Si	0.0099	0.0171
FeO	75.1	74.44	0.3315	Fe+2	0.3315	0.5742
Fe2O3	n.d.	n.d.	0.3315	Fe+3	0.663	1.1484
Al2O3	1.382	1.3699	0.0126	Al	0.2514	0.4354
				O	2.3094	
sum	100.89	100				2.69

GRAIN 8, 1tm

	1	2	3		4	5
MnO	0.331	0.361	0.0051	Mn	0.0051	0.01
TiO2	16.625	18.134	0.227	Ti	0.227	0.4445
SiO2	1.968	2.147	0.0487	Si	0.0487	0.0954
FeO	71.594	78.091	0.3623	Fe+2	0.3623	0.7094
Fe2O3	n.d.	n.d.	0.3623	Fe+3	0.7246	1.4188
Al2O3	1.162	1.267	0.0124	Al	0.0248	0.0486
				O	2.0429	
sum	91.68	100				2.73

GRAIN 8, 2tm

	1	2	3		4	5
MnO	1.913	1.983	0.028	Mn	0.028	0.0546
TiO2	25.73	26.669	0.3338	Ti	0.3338	0.6505
SiO2	1.003	1.04	0.0236	Si	0.0236	0.046
FeO	67.413	69.873	0.3242	Fe+2	0.3242	0.6318
Fe2O3	n.d.	n.d.	0.3242	Fe+3	0.6484	1.2636
Al2O3	0.42	0.435	0.0043	Al	0.0086	0.0168
				O	2.0525	
sum	96.479	100				2.66

GRAIN 8, 3tm

	1	2	3		4	5
MnO	0.328	0.36	0.0051	Mn	0.0051	0.0102
TiO2	13.056	14.338	0.1794	Ti	0.1794	0.3576
SiO2	1.576	1.731	0.0393	Si	0.0393	0.0783
FeO	74.996	82.359	0.3821	Fe+2	0.3821	0.7617
Fe2O3	n.d.	n.d.	0.3821	Fe+3	0.7942	1.5832
Al2O3	1.104	1.212	0.0119	Al	0.0238	0.0474
				O	2.0066	
sum	91.06	100				2.84